



International Federation for Heat Treatment and Surface Engineering 20th Congress  
Beijing, China, 23-25 October 2012

## Characterizing an in situ $\text{TiB}_2$ particulates reinforced aluminium-based composite and its heat treatment

Fei Xie<sup>a, b, \*</sup>, Zhong-hua Xue<sup>a</sup>

<sup>a</sup> Materials Science and Engineering School, Changzhou University, Changzhou 213164, China

<sup>b</sup> Key Laboratory of Advanced Metallic Materials of Changzhou City, Changzhou University, Changzhou 213164, China

### Abstract

Metal matrix composites were fabricated in an Al-6Cu-0.2Mg-1Mn matrix reinforced by particulates of in-situ  $\text{TiB}_2$  from a reaction process via  $\text{K}_2\text{TiF}_6$  and  $\text{KBF}_4$  salts in the matrix. Different percentage of the  $\text{TiB}_2$  particulates, 1 wt-%, 3 wt-% and 5 wt-%, respectively, was employed for the composite. A series of heat treatments comprised of solution treatment and aging were carried out on the composites. Phases, microstructures and Vickers' hardness were revealed for the differently treated composites and Al-6Cu-0.2Mg-1Mn alloy. The results showed that the in-situ  $\text{TiB}_2$  particulates could improve the structure of the matrix by retarding a directional growth of the matrix grains and forming isometric grains in the matrix. Remelting the composite with 3 wt-%  $\text{TiB}_2$  tended to weaken  $\text{TiB}_2$  particulates' clustering. A significant effect on the refinement of the grains was observed when the content of  $\text{TiB}_2$  particulates was increased from 0 to 5 wt-%. And the Vickers' hardness of the differently treated composites with 3 wt-% or 5 wt-%  $\text{TiB}_2$  was higher than that of the corresponding Al-6Cu-0.2Mg-1Mn alloys. The composite's precipitation rate was accelerated with the increase of the content of  $\text{TiB}_2$  particles during aging at 170°C.

© 2013 The Authors. Published by Elsevier B.V. Open access under [CC BY-NC-ND license](#).  
Selection and peer-review under responsibility of the Chinese Heat Treatment Society

Keywords: Aluminum matrix composites;  $\text{TiB}_2$  particulates; In situ; Microstructure; Vickers' hardness

### 1. Introduction

Automotive and aerospace industries have extremely high demands on strength to density ratio of materials. Casting aluminium alloy has wide applications in the automotive and aerospace industries for its good mechanical properties, high workability, good surface finish, excellent corrosion resistance, and, especially, high strength to density ratio (Rooy, 1992). Adding proper reinforcements, such as particulates, whiskers, platelets, with proper way

\* Corresponding author. Tel.: +86 13401316979 (mobile).  
E-mail address: [xiefei@cczu.edu.cn](mailto:xiefei@cczu.edu.cn)

to form a composite can further improve aluminium alloy's properties. In situ composites reinforced with particulates have advantages over ex-situ composites in grain refinement, uniform distribution of reinforcements, excellent bond between the reinforcement and matrix, and economy of fabrication. Hard ceramic particulates such as  $\text{TiB}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiC}$  have been employed as reinforcements, among which  $\text{TiB}_2$  has been paid special attention for its stability in aluminium based matrix (Rawal, 2001; Kaczmar et al., 2000; Sivaprasad et al., 2008; Daniel et al., 1997). Like in many types of aluminium alloys, heat treatment also plays an important role in resulting high strength for aluminium alloy based composites (Bartels et al., 1997; El-Baradie et al., 1998).

In order to improve the strength of casting aluminium alloy, this study fabricated a casting aluminium alloy and the aluminium alloy matrix based composite reinforced by in situ  $\text{TiB}_2$  particulates. Characterizations were made on microstructures, properties and heat treatments of the alloy and the composite.

## 2. Experimental details

Aluminium alloy denoted as Al-6Cu-0.2Mg-1Mn (6 wt-%Cu, 0.2 wt-% Mg, 1 wt-% Mn, bal. Al ) was prepared at 850°C in an electrical furnace by using 99.9% pure Al, 99.9% pure Cu, 99% pure Mg and 99% pure Mn elements. Aluminium alloy matrix composites reinforced by particulates of in situ  $\text{TiB}_2$  were fabricated by adding potassium hexafluorotitanate ( $\text{K}_2\text{TiF}_6$ ) and potassium tetrafluoroborate ( $\text{KBF}_4$ ) into the melted Al-6Cu-0.2Mg-1Mn alloy at 950°C in an atomic ratio in accordance with Ti/B and the desired  $\text{TiB}_2$  amount in the composites. The desired  $\text{TiB}_2$  content in the composites was 1 wt-%, 3 wt-% and 5 wt-%, respectively. The  $\text{K}_2\text{TiF}_6$  and  $\text{KBF}_4$  salts were pre-heated at 250°C for 1 h before being added into the melted Al-6Cu-0.2Mg-1Mn. After full reactions of the salts in the molten alloy, the melt was cooled to 850°C and stirred for a long time. Then the melt was cooled to 750°C and kept at the temperature for 1 h before casting. Metal moulds were used for the casting of the Al-6Cu-0.2Mg-1Mn alloy and the composites. The composite with 3 wt-%  $\text{TiB}_2$  was remelted with more stirring to investigate the influence of remelting on the composite.

The cast ingots were sectioned into specimens with sizes of 15mm×15mm×15mm for further investigation. Solution treatment was carried out at 505°C for 2 h followed by water quenching. Aging was carried out at 170°C.

Microstructures of the aluminium alloy and the in situ composites were examined with an optical microscope. Phases of the aluminium alloy and the in situ composites were identified by a D/max 2500 PC X-ray diffractometer with Cu  $K\alpha$  radiation operated at 40 kV and 100mA. The specimens' hardness was measured by a Vickers' hardness tester at a load of 300g for 20s. The average of 4 to 6 measurements made in different points on each specimen was employed as the specimens' hardness discussed in the present study.

## 3. Results and discussions

### 3.1. Phases

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-casted Al-6Cu-0.2Mg-1Mn and its composite with 5 wt-% in situ  $\text{TiB}_2$  particles. XRD analysis showed that the Al-6Cu-0.2Mg-1Mn alloy consisted mainly of aluminium and  $\text{CuAl}_2$  phases. The XRD patterns for the composite showed  $\text{TiB}_2$  peaks as well as peaks for aluminium and  $\text{CuAl}_2$  phases, indicating that Ti and B atoms released from the salts had formed  $\text{TiB}_2$  according to an assumed reaction below.



No peak for  $\text{TiAl}_3$  was found, although some researchers suggested that  $\text{TiAl}_3$  formed during the formation of the in situ  $\text{TiB}_2$  particles (Bartels et al., 1997; Mohanty et al., 1995). It was also observed that the intensities of  $\alpha(\text{Al})$  were much greater in (311) plane and especially in (111) plane than in any other planes in the XRD pattern of Al-6Cu-0.2Mg-1Mn specimen. However, no such phenomenon is observed in the XRD result for the composite. The

investigation result meant that preferred orientation of  $\alpha(\text{Al})$  grains existed in the as-casted Al-6Cu-0.2Mg-1Mn specimens rather than in the composite.

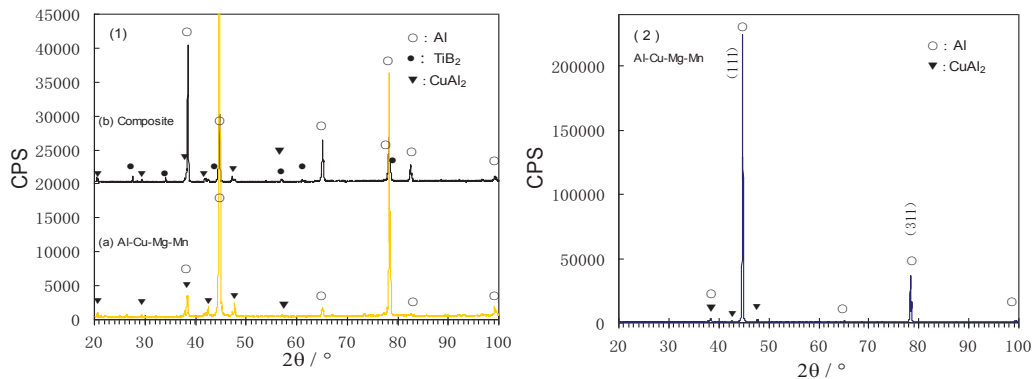


Fig. 1. XRD spectra of as-casted (1) Al-Cu-Mg-Mn alloy and composite with 5 wt-% in situ  $\text{TiB}_2$  particles, (2) Al-Cu-Mg-Mn

### 3.2. Microstructures

Although the alloying element Mn has a function of refining grains in aluminium alloy, the as-casted Al-6Cu-0.2Mg-1Mn had a coarse dendritic structure and the  $\alpha(\text{Al})$  grains had a strong orientation, as shown in Fig. 2a. Figs. 2b to d give microstructures of the as-casted composites with an in situ  $\text{TiB}_2$  content of 1 wt-%, 3 wt-% and 5 wt-%, respectively. With the addition of  $\text{TiB}_2$ , the morphology of the matrix has turned from the dendritic feature to equiaxed grains. No preferred orientation of  $\alpha(\text{Al})$  grains was found, which verified what was obtained by XRD (see Fig. 1). And the matrix becomes more finer with the increase of the  $\text{TiB}_2$  content. It has been well known that the  $\text{TiB}_2$  particulates are the most active nucleants which can be the nuclei for the formation of  $\alpha(\text{Al})$  grains during casting (Cibula, 1951; Johnsson, 1993), although there have been different opinions on the function of the  $\text{TiB}_2$  (Mohanty et al., 1995; Guzowski, et al., 1987). Thus the number of the crystal nuclei in the melts is increased.  $\text{TiB}_2$  particulates adhered to the solidified  $\alpha(\text{Al})$  grains also have a function on retarding the growth of the  $\alpha(\text{Al})$  grains. As a result of the two effects of  $\text{TiB}_2$  particulates, the  $\alpha(\text{Al})$  grains in the as casted composites were refined.

The  $\text{TiB}_2$  particulate tended to adhere to  $\text{CuAl}_2$  and even formed a cluster (Figs 2b to d and Fig. 3a). Remelting the composite with more mechanical stirring weakened the clustering extent (Fig. 3b). There was no change to the size of substrate  $\alpha(\text{Al})$  grains.

Figure 4 shows microstructures of the Al-6Cu-0.2Mg-1Mn alloy and the composites after 4h solution treatment at 505°C. Compared with those as-casted specimens, the former continuous / net-like  $\text{CuAl}_2$  phase became separated particles or less continuous sticks as a result of partial dissolution of  $\text{CuAl}_2$  phase into the matrix. There were slight changes to the distribution and the amount of  $\text{TiB}_2$  particulates, as the stable  $\text{TiB}_2$  did not dissolve in the matrix by heating at 505°C.

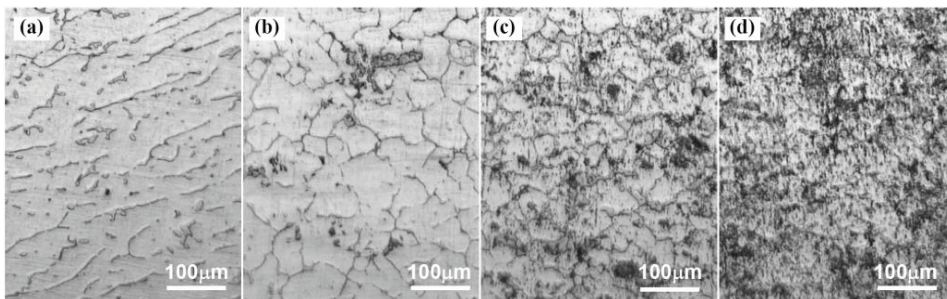


Fig. 2. Microstructures of as-casted (a) Al-6Cu-0.2Mg-1Mn alloy and composites with  $\text{TiB}_2$  content of (b) 1 wt-%, (c) 3 wt-%, and (d) 5 wt-%.

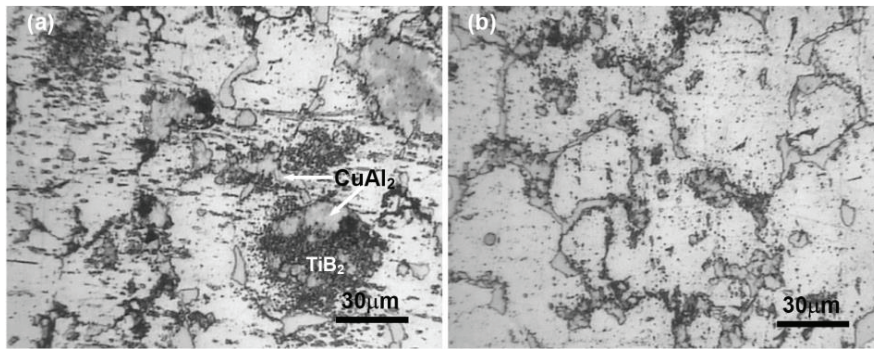


Fig. 3. Microstructures of an (a) un-remelted and (b) remelted composite with  $\text{TiB}_2$  content of 3 wt-%.

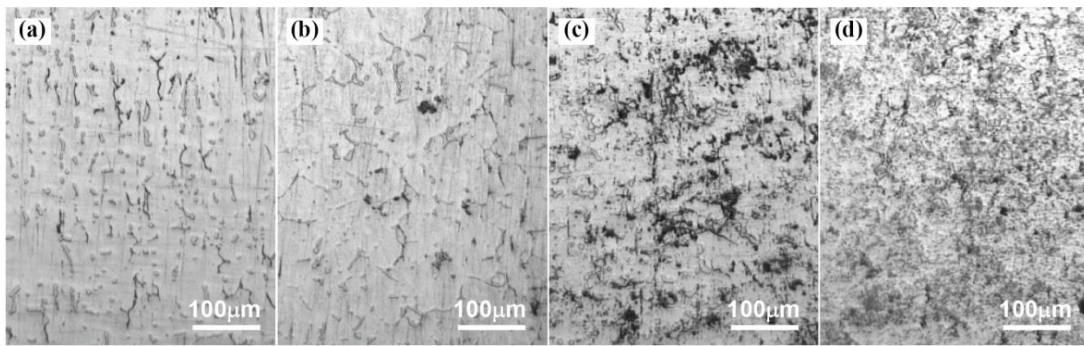


Fig. 4. Microstructures of solution treated (a) Al-6Cu-0.2Mg-1Mn alloy and composites with  $\text{TiB}_2$  content of (b) 1 wt-%, (c) 3 wt-%, and (d) 5 wt-%.

### 3.3. Vickers' hardness

Table 1 gives Vickers' hardness of the as-casted and solution-treated Al-6Cu-0.2Mg-1Mn alloy and the composites. Figure 5 demonstrates age hardening curves of the five materials. It can be seen that there was slight difference in hardness at different treating states between the Al-6Cu-0.2Mg-1Mn alloy and the composites when the content of  $\text{TiB}_2$  particles in the composite was low. However, hardness was shifted to a higher value with increasing the  $\text{TiB}_2$  particle content. When the content of  $\text{TiB}_2$  particles reached 5 wt-%, the composite's hardness was much higher at all states than that of the corresponding Al-6Cu-0.2Mg-1Mn alloy. Although hardness peaks were reached after 10 h aging for the five materials, hardness for the un-remelted composites with 3 wt-% and 5 wt-%  $\text{TiB}_2$  particles after 6 h aging had already quite been close to the peak harness. Hardness increased more quickly for the composites with 3 wt-% and 5 wt-%  $\text{TiB}_2$  particles than that for the rest two materials during aging. The results meant that aging precipitation growth was accelerated when there were enough  $\text{TiB}_2$  particles. Similar phenomena were observed by other researchers in aging of composites reinforced with  $\text{TiB}_2$  or SiC particles (Daniel et al., 1997; El-Baradie et al., 1998; Suresh et al., 1989).

Re-melting also caused an increase in hardness of the composite at various states. It should be mainly attributed to the improvement of distributions of  $\text{TiB}_2$  particles and alloying elements.

Table 1 Vickers' hardness of the as-casted and solution-treated samples, HV0.3



Materials	As-casted	Solution-treated
Al-6Cu-0.19Mg-1Mn	70.4	83.3
Al-6Cu-0.19Mg-1Mn+1%TiB <sub>2</sub>	67.5	83.6
Al-6Cu-0.19Mg-1Mn+3%TiB <sub>2</sub>	74	84.7
Al-6Cu-0.19Mg-1Mn+5%TiB <sub>2</sub>	84.2	94.3
Remelted Al-6Cu-0.19Mg-1Mn+3%TiB <sub>2</sub>	82.3	90.2

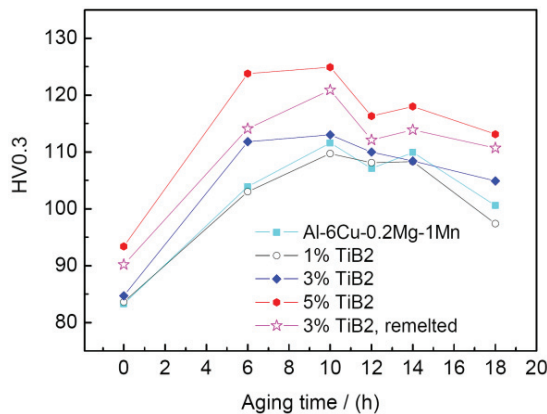


Fig. 5. Age hardening curves of differently prepared specimens aged at 170°C

### 3.4. Discussions

When the nominal TiB<sub>2</sub> particulate content was low, such as 1 wt-%, the dispersing hardening effect from the TiB<sub>2</sub> particulate was not clear. The TiB<sub>2</sub> particles at such low content showed effect mainly in refining grains by providing more crystal nucleus during the solidification. When the TiB<sub>2</sub> particulate content was increased to 3wt-% or 5wt-%, the TiB<sub>2</sub> particulate showed effects not only in refining the composites to small equal-axial grains but also in dispersing hardening to improve the composites' hardness and strength.

It is well known that age hardening in aluminium alloy involves the formation of coherent clusters of solute atoms and some metastable phases which are coherent, semi-coherent or incoherent with the matrix (Rooy, 1992). The growth of those clusters and metastable phases is controlled by diffusion. Therefore, the changes observed in the present study as a function of aging time and TiB<sub>2</sub> content (Fig. 5), were, in fact, the changes in the growth of those clusters and metastable phases, which should be attributed to an increase in diffusivity in the alloys. It was assumed that pipe diffusion should account for the increase in diffusivity (Daniel et al., 1997). Pipe diffusion is a kind of diffusion through dislocation. A large amount of plastic strain develops due to the thermal mismatch of TiB<sub>2</sub> particulates with the matrix when the composite is quenched from the solutionizing temperature. The strain is accommodated by the generation of extra dislocations leading to a higher dislocation concentration around the reinforcement particles (Bartels, et al., 1997; El-Baradie et al. 1989). Suresh et al. (1989) measured the dislocation density and showed that it was approximately  $6 \times 10^9 \text{ cm}^{-2}$  in the unreinforced alloy, whereas in the composite it could be as high as  $2 \times 10^{10} \text{ cm}^{-2}$ .

Remelting the composite improved the TiB<sub>2</sub>'s distribution, and the distribution of dislocations caused by the reinforcement particulate was also improved. Therefore, those clusters and metastable phases formed during aging will be more evenly merged, leading higher aging hardness.

#### 4. Conclusions

(1) The in situ  $\text{TiB}_2$  particulates have functions in retarding the growth of dendritic grain of the matrix, refining grain structure, leading to equal-axial matrix grains.

(2) When the  $\text{TiB}_2$  particulate content was increased to 5wt-%, the  $\text{TiB}_2$  particulate showed effects not only in refining the matrix to small equal-axial grains but also in dispersing hardening to improve the composites' hardness and strength. The solutionized composite's precipitation rate was accelerated during aging at 170 °C with the increase of the content of  $\text{TiB}_2$  particles.

(3) Remelting the composite with 3 wt-%  $\text{TiB}_2$  improved the distribution of  $\text{TiB}_2$  and increased the composite's hardness.

#### References

- Bartels C., Raabe D., Gottstein G., Huber U. 1997. Investigation of the precipitation kinetics in an Al6061/ $\text{TiB}_2$  metal matrix composite. *Materials Science and Engineering A* 237, 12–23.
- Cibula A., 1951. The grain refinement of aluminum alloy castings by additions of titanium and boron. *Journal of the Institute of Metals* 80, 1–16.
- Daniel B. S. S., Murthy V. S. R., Murty G. S., 1997. Metal-ceramic composites via in-situ methods. *Journal of Materials Processing Technology* 68, 132–155.
- El-Baradie Z. M., El-Shahat O. A., Abd El-Azim A. N., 1998. Accelerated aging processes in SiC-7020 aluminium composite. *Journal of Materials Processing Technology* 79, 1–8.
- Guzowski M. M., Sigworth G. K., Sentner D. A., 1987. The role of boron in the grain. *Metallurgical Transactions A-Physical Metallurgy and Materials Science* 18A 603–619.
- Johnsson M., Backerud L., Sigworth G. K., 1993. Study of the mechanism of grain refinement of aluminum after additions of Ti- and B-containing master alloys. *Metallurgical Transactions A-Physical Metallurgy and Materials Science* 24A, 481–491.
- Kaczmar J. W., Pietrzak K., Włosiński W., 2000. The productions and application of metal matrix composite materials. *Journal of Materials Processing Technology* 106, 58–67.
- Mohanty P. S., Gruzleski J. E., 1995. Mechanism of grain refinement in aluminium. *Acta Metallurgica et Materialia* 43, 2001–201.
- Rawal S., 2001. Metal-Matrix Composites for Space Applications. *Journal of the Minerals, metals and Materials Society* 53, 14–17.
- Rooy E. L., 1992. Introduction to aluminum and aluminum alloys. In: *ASM Handbook, Vol. 2, Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*, ASM International, Materials Park, Ohio, pp. 90–115.
- Sivaprasad K., Kumaresh Babu S. P., Natarajan S., Narayanasamy R., Kumar B. Anil, Dinesh G., 2008. Study on abrasive and erosive wear behaviour of Al/6063  $\text{TiB}_2$  in situ composites. *Materials Science and Engineering A* 498, 495–500.
- Suresh S., Christman T., Sugimura Y., 1989. Accelerated aging in cast Al alloy-SiC particulate composites. *Scripta Metallurgica* 23 1599–1602.